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Author(s): Rajendra U. Vaidya, Partha Rangaswamy, Darryl P. Butt, Amit Misra, David E. Gallegos, Richard G. Castro, and John J. Petrovic

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Use of a Cobalt Based Metallic-Glass in Joining $MoSi_2$ to Stainless Steel

Rajendra U. Vaidya, Partha Rangaswamy, Darryl P. Butt*, Amit Misra,
David E. Gallegos, Richard G. Castro, and John J. Petrovic

Materials Science and Technology Division,
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

*Department of Materials Science and Engineering
University of Florida, Gainesville, FL 32611, USA

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Abstract

The successful use of a cobalt-based metallic-glass in joining molybdenum disilicide ($MoSi_2$) to stainless steel 316L was demonstrated. Such joints are being investigated for sensor tube applications in glass melting operations. The cobalt-based metallic-glass (METGLAS^{TM} 2714A) was found to wet the $MoSi_2$ and stainless steel surfaces and provide high quality joints. Joining was completed at 1050 ^oC for 60 minutes in two different ways; either by feeding excess braze into the braze gap upon heating or by constraining the $MoSi_2$/stainless steel assembly with an alumina (Al_2O_3) fixture during the heating cycle. These steps were necessary to ensure the production of a high quality void free joint. Post-brazing metallographic evaluations coupled with quantitative elemental analysis indicated the presence of a Co-Cr-Si ternary phase with CoSi and $CoSi_2$ precipitates within the braze. The residual stresses in these molybdenum disilicide ($MoSi_2$)/stainless steel 316 L joints were evaluated using X-ray diffraction and instrumented indentation techniques. These measurements revealed that significant differences are induced in the residual stresses in $MoSi_2$ and stainless steel depending on the joining technique employed. Push-out tests were carried out on these joints to evaluate the joint strength.

Introduction

Molybdenum disilicide ($MoSi_2$) is a potential high temperature structural material owing to its excellent oxidation resistance, high melting temperature (2030 ^oC), relative low density (6.24 g/cm^3), high thermal conductivity (52 W/mK),a brittle to ductile transition near 1000˚C, and stability in a variety of corrosive and oxidative environments [1-5]. Some potential uses for $MoSi_2$ include furnace components, gas burners and ignitors, gas injection tubes, high temperature nozzles, temperature sensor sheaths, and periscope sight tubes [1, 2, 6].

In order for $MoSi_2$ to be used in many of the aforementioned applications it must first be joined to other materials, in particular to ferrous alloys like stainless steels (see Figure 1). However, direct bonding of $MoSi_2$ to stainless steels is difficult due to the large differences in the coefficients of thermal expansion (CTE) between $MoSi_2$ and stainless steel. The large thermal expansion mismatch coupled with the necessity of using high joining temperatures (in the case of refractory brazes) results in large residual stresses, and leads to joint failure upon

cooling. Low temperature brazing techniques and the use of ductile interlayers of intermediate CTE can alleviate the problem of large thermal stresses developed upon cooling from the bonding temperatures [7-9]. However, the addition of the interlayers adds to the cost and complexity of the joining process.

Figure 1. Potential application for the metallic-glass brazes joint. The $MoSi_2$ injector tube (bottom right of the figure) is joined to a stainless-steel adapter. The complexity of the joint makes the use of metallic-glass foils very attractive.

From a joining standpoint, use of metallic-glasses as brazing foils provides a number of practical advantages. The use of metallic-glasses reduces the size of the brazement gaps as those used with brazing pastes and powders, to achieve complete filling of the braze cross-section. The high flexibility and ductility of these amorphous foils allows them to be used as a preplaced preform. These metallic-glasses also melt over a narrow temperature range (during transient heating). The result is less erosion of the base materials being joined, lower sensitization of the base materials due to the shorter brazing times, absence of organic solvents (as with brazing pastes), and a more uniformly brazed joint. Furthermore, these foils have a significantly smaller amount of surface oxide film, unlike the gas-atomized powders used in filler brazes. These surface oxides prevent fusion of individual particles and may result in non-uniform melting.

Although metallic-glasses have been used as brazes in various metal-metal systems, there have been no other studies in the literature demonstrating their use in ceramic-metal joining. We have been the first to demonstrate the successful use of a cobalt-based metallic-glass in joining $MoSi_2$ to stainless steel [10]. Mechanical push-out tests coupled with detailed metallographic evaluations revealed high quality joints with good mechanical strength. We were particularly interested in evaluating the performance of this system because of its potential use in the glass melting industry where $MoSi_2$ is being developed as a protective sensor sheath material [11]. For such applications it is imperative for the $MoSi_2$ to be operating above the 500-550 ^oC temperature range where pesting (oxidation) can occur. We are proposing to join $MoSi_2$ to stainless steel in a region where the temperature of the protective $MoSi_2$ sheath is above 600 ^oC, while maintaining the stainless steel below its sensitization temperature (~800 ^oC).

This paper discusses various aspects of the joining process. Measurements of the residual stresses in these $MoSi_2$-stainless steel joints are also included. We realize that the $MoSi_2$/stainless steel joints (in the applications mentioned earlier) will only be subjected to temperature excursions between 600 ^oC and room temperature, and residual stress relaxation will occur during the heating cycle (in the application). However, measurement of the residual stresses developed upon cooling from the brazing temperature provides us with data at the

extreme limits of the application. Furthermore, it is particularly important to determine the residual stresses developed in the $MoSi_2$ upon cooling from the brazing temperature in order to predict joint strength and reliability. We have used two different techniques to evaluate the residual stresses; X-ray diffraction and instrumented indentation. The results of these measurements are presented herein.

Experimental

Materials

Commercial $MoSi_2$ Super Kanthal™ (Kanthal AB, Sweden) extruded injector tubes were used in the joining experiments. The 12 mm diameter $MoSi_2$ tubes (with a 2.5 mm diameter hole in the center) were sliced 2.5 mm thick into disks and their surfaces were ground to -600 grit. The porosity in the $MoSi_2$, as determined by image analysis, was ~14 v/o. The stainless steel 316 L bar stock material was machined in the form of rings, with an outside diameter of 19 mm and an inside diameter of 12.1 mm. The thickness of the rings was 2.5 mm. All of the stainless steel sample surfaces were polished (to –600 grit). The cobalt-based metallic-glass consisted of 15 %Si, 14%B, 4%Fe, and 1%P. This particular composition of metallic-glass was selected (out of a variety of compositions) based on its wetting and high temperature capabilities. The metallic-glass was obtained from Allied Signal, Inc. (New Jersey, USA). The metallic-glass ribbons had a nominal width of 50 mm and a thickness of 25 μm. The metallic-glass ribbons were cut to size using a pair of precision shears. All of the materials were ultrasonically cleaned in acetone followed by deionized water, prior to joining.

Brazing Procedure

Two different experimental braze setups were used. For the *unconstrained* samples, the brazing foil was placed between the stainless steel ring and $MoSi_2$ tube. The height of the brazing foil was cut to twice (~5 mm) that of the ring thickness in order to provide the extra braze volume to feed into the braze gap on heating. The entire assembly was placed into a tube furnace which was vacuum purged with ultra high purity Ar-6% H_2 gas (three times) at room temperature and again at 250 ^{o}C to remove oxygen and absorbed water from the furnace and brazing assembly. The furnace was then purged continuously with Ar-6% H_2 gas. The ultra high purity Ar-6% H_2 gas was gettered by passing it first through calcium sulfate at room temperature and then 99.9% pure copper at 650 ^{o}C. The joints were completed by heating the assemblies from 250 ^{o}C, at 5 ^{o}C/min to the brazing temperature of 1050 ^{o}C, (which was ~10 ^{o}C above the braze melting temperature) and was held for 60 minutes before cooling at 2 ^{o}C/min to room temperature.

An Al_2O_3 fixture was used for making the *constrained* samples. The fixture consisted of an Al_2O_3 holder with a recess. The stainless steel ring, $MoSi_2$ tube and the brazing foil were arranged within this recess. The diameter of the recess was 19.13 mm. This diameter was selected so as to apply a constraint on the assembly during the heating cycle. The constraint prevented excessive expansion of the stainless steel ring on heating, thereby ensuring contact between the stainless steel, $MoSi_2$, and the metallic-glass foil during the brazing process. No additional braze material was added anytime during this joining process. The heating and cooling cycles employed in the brazing process were identical to the one described earlier. The unjoined stainless steel and $MoSi_2$ control samples used for comparison were subjected to identical heat treatments and environments as those used during the joining process.

X-ray Diffraction

Residual stresses were determined using conventional X-ray diffraction [12]. A residual stress/texture goniometer using copper Kα radiation produced by a 18 kW rotating anode was employed for recording diffraction data. The shallow penetration depth (≤ 20 micrometers) in $MoSi_2$ and stainless steel justified use of the classical "d vs. $\sin^2\psi$" approach employing the (241) and (331) peaks in $MoSi_2$ and stainless steel 316L, respectively. Stress measurements were made by collimating the incident X-ray beam to obtain a spot size of 2 mm on the specimens. The XRD elastic constants used were calculated from bulk values (E = 380 GPa, $\upsilon = 0.3$ for $MoSi_2$, and E =195 GPa, $\upsilon = 0.25$ for stainless steel). The hoop stresses were measured at 16 positions (8 each in stainless steel and $MoSi_2$) along the diameter by stepping in increments of 0.5 mm. The sampling areas overlapped by 0.5 mm giving a better spatial resolution. Preliminary diffraction patterns of the $MoSi_2$ and stainless steel, ranging from 20 to 160 degrees of 2θ, revealed no evidence of preferred orientation. From the diffraction patterns a suitable diffraction peak (≥ 140^o of 2θ) was selected.

Instrumented Indentation

Residual stresses in the stainless steel rings were determined using the instrumented sharp indentation technique developed by Suresh and Giannakopoulos [13]. This technique could not be used for $MoSi_2$ due to cracking during indentation. An instrumented microhardness indentation machine with maximum load capacity of 30 N was used with a Vickers indenter tip. The typical *load-controlled indentation cycle* used was as follows: load at the rate of 10 N/min to a maximum load of 25 N, hold at maximum load for 20 s, and unload at the rate of 30 N/min. Several indents were made as a function of distance from the interface. For the unconstrained joint only, the residual stresses were also estimated using depth-controlled indentation, and the results were compared to those from the load-controlled experiments. The typical *depth-controlled indentation cycle* used was as follows: load at the rate of 10 N/min to a maximum depth of 20 μm, hold at maximum load for 20 s, and unload at the rate of 30 N/min. Stainless-steel 316L rings, in the unjoint state, were used as the reference to obtain the zero residual stress indentation response. All samples were polished to 0.05 μm finish prior to indentation testing.

It must be noted here that the indentation experiments provide an in-plane "average stress" (average of hoop and radial components). Although we only measured the hoop component of the residual stress by X-ray diffraction, three element thermoelastic continuum models (for concentric cylinders) used in residual stress evaluation [14,15], have indicated that the hoop and radial components to be very similar, when the thickness of the cylinders is significantly smaller than the diameter of the cylinders.

Push-out tests

Details of the experimental setup used in the push-out tests have been documented in our previous study [10]. The normal force applied to the $MoSi_2$ in the center of the sample was balanced with the shear force at the $MoSi_2$-stainless steel interface, and the shear strength of the joint was evaluated therefrom. The maximum shear stress at the interface τ_{max} was evaluated using the equation

$$\tau_{max} = F_{max}/(2\pi dh) \qquad (1)$$

where, F_{max} is the maximum pushout load(force), d is the inside diameter of the stainless steel ring and h is the height (or thickness) of the sample. The push-out tests were performed in an

Instron machine using a cross head speed of 0.05 mm/min. Five samples were tested for each condition (constrained and unconstrained).

It is important to note that the push-out test used was not a standardized test, and was used for screening purposes only. The stresses developed at the interface may not be pure shear (may have a bending component).

Results

Figure 2 illustrates a polished section of a $MoSi_2$-stainless steel 316L joint. These joints were free of voids and cracks. The brazing process was reactive and resulted in the formation of intermetallic $CoSi_2$ precipitates in a Co-Si-Cr ternary matrix. The microstructure also consisted of some Co and Si rich regions within the braze. A number of joined samples were heated to 600 ^oC and held for times ranging between 60 minutes and 240 minutes. A few samples were also cycled between 600 ^oC and room temperature. The microstructure of the braze was observed to be very stable with no significant evolution.

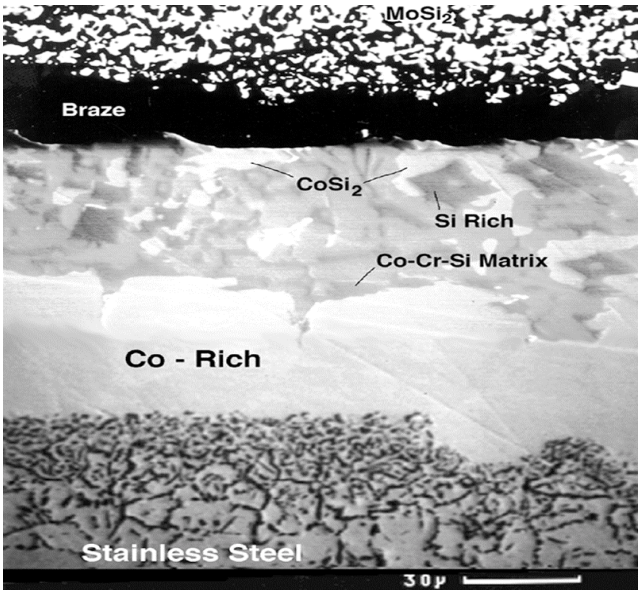

Figure 2. Optical micrograph of the brazed joint. The stainless steel is in the bottom of the figure, and the $MoSi_2$ is at the top. Note the various phases in the braze.

Some important observations were noted in the process of measuring the residual stresses in these $MoSi_2$/stainless steel joints. The compressive residual stress in the $MoSi_2$ was greater in the unconstrained samples versus the constrained samples, although the magnitude of these stresses was smaller than the fracture strength of the $MoSi_2$. This can be accounted by the fact that additional braze is fed into the braze gap on heating in the unconstrained samples. Upon cooling (after the joint is completed), the stainless steel begins to shrink onto the braze and $MoSi_2$. However, the volume of the braze in the gap is twice of what it was at the beginning of the joining process, and higher compressive stresses are induced in the $MoSi_2$. Further evidence of these compressive stresses lie in the fact that the peak stresses corresponding to the push-out loads for the joints made in the unconstrained state (mean 145.4 MPa) are significantly higher than those for the joints made using an external constraint (mean 72.3 MPa).

In the case of the constrained samples, the evolution of the residual stresses is more complex and occurs during the heating and cooling cycles. During the heating cycle, the stainless steel

expands more than the braze and $MoSi_2$. However, expansion of the stainless steel ring is prevented by the presence of the external Al_2O_3 holder, which has a significantly smaller CTE as compared to stainless steel. As a result residual stresses develop in the stainless steel during the heating cycle. Part of these stresses relax as a result of plastic deformation. Upon cooling, the stainless steel shrinks back to its original dimension. The indentation studies indicate higher tensile residual stresses in the stainless steel in joints made using the external constraint. However, the residual stresses in the $MoSi_2$ appear to be less affected by the presence of the external constraint. The residual stress measurements completed using X-ray diffraction and instrumented indentation were consistent and complimentary.

Although we have not completed any studies to model the stresses in these $MoSi_2$/stainless steel joints, these experimental measurements have provided us with insight into the evolution of residual stresses in such joint systems, and some of the results are not intuitively obvious. Practical factors such as available space where the joint has to be made and equipment availability will dictate recommending one joining technique over another. The residual stresses in $MoSi_2$ are larger in the unconstrained state, but these values are still not large enough to cause catastrophic failure of $MoSi_2$. We plan to complete a detailed modeling study on these complex joints in the future.

Conclusions

We successfully measured the residual stresses in a $MoSi_2$/stainless steel joint brazed with a cobalt-based metallic glass braze, using X-ray diffraction and controlled indentation. The residual stresses developed upon cooling in joints in the unconstrained state (but with extra braze), in the $MoSi_2$, were higher as compared to the constrained state. Higher tensile residual stresses developed in the stainless steel when the joining was completed under constrained conditions. The interfacial joint strength, as measured by push-out tests, indicated significantly higher (twice) values for the joints made without any external constraint. The joint strength and residual stress values are within acceptable values for the sensor sheath applications.

References:

1. J.J. Petrovic, *MRS Bull.* ,**18[7]**, (1993) 35-37.
2. J.J. Petrovic, and A. K. Vasudevan, *Mater. Sci. Eng.,* **A261** (1999) 1-12.
3. T.C. Chou, and T.G. Nieh, *J. Mater. Res*., **8** (1993) 214-219.
4. D.A. Berztiss, R.R. Cerchiara, E.A. Gulbransen, F.S. Pettit, and G.H. Meier, *Mater. Sci. and Eng*., **A155** (1992) 165-168.
5. J.J. Petrovic, *Mater. Sci. and Eng*., **A192-193** (1995) 31-35.
6. A. Bartlett, R. Castro, H. Kung, D.P. Butt, and J.J. Petrovic, *Industrial Heating, J. of Thermal. Tech.*, **63** (1996) 33-37.
7. C. R. Hubbard, S. Spooner, S. A. David, B. H. Rabin, and R. L. Williamson, *Mater. Sci. Eng,* **A211** (1996) 45-49.
8. R. U. Vaidya, D. P. Butt, S. D. Conzone, and A. H. Bartlett, *Ceram. Trans.*, **77** (1996) 63-71.
9. R. U. Vaidya, P. Rangaswamy, M. A. M. Bourke, and D. P. Butt, *Acta Metall. Mater*., **46** (1998) 2047-2058.
10. R. U. Vaidya, P. Rangaswamy, R. G. Castro, J. J. Petrovic, and D. P. Butt, *J. Mater. Eng. Perf*., **9** (2000) 280-288.
11. AIM Annual Report 1998, Los Alamos National Laboratory.
12. I. C. Noyan and J. B. Cohen, "Residual Stress-Measurement by Diffraction and Interpretation", Springer-Verlag, New York, 1987.

13. S. Suresh and A. Giannakopoulos, *Acta Metall. Mater*., **20** (1998) 5755.

For further information contact: Rajendra Vaidya, MS E 574, NMT-16, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. Tel. (505)-665-8130 e-mail: raj@lanl.gov